

10/083 781

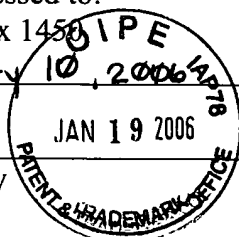
COFC

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REQUEST FOR CERTIFICATE OF CORRECTION UNDER 37 CFR 1.322
Docket No. USF-104XC1
Patent No. 6,965,026

Jenna M. Morrison

Jenna M. Morrison, Patent Attorney



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : Michael J. Zaworotko, Brian Moulton
Issued : November 15, 2005
Patent No. : 6,965,026
For : Nanoscale Faceted Polyhedra

Mail Stop Certificate of Corrections Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Certificate
JAN 24 2006
of Correction

REQUEST FOR CERTIFICATE OF CORRECTION
UNDER 37 CFR 1.322 (OFFICE MISTAKE)

Sir:

A Certificate of Correction (in duplicate) for the above-identified patent has been prepared and is attached hereto.

In the left-hand column below is the column and line number where errors occurred in the patent. In the right-hand column is the page and line number in the application where the correct information appears.

Patent Reads:

Column 3, line 39:

“subject, invention”

Column 5, line 44:

“J = -350 c⁻¹ and”

Application Reads:

Page 4, Paragraph 0020, line 2:

--subject invention--.

Page 7, Paragraph 0045, line 4:

-- J = -350 cm⁻¹ and --.

JAN 24 2006

Column 6, line 62:

“carboxylate ii that”

Column 8, line 21:

“criterion g include”

Column 8, line 55:

“(M¹₆A¹₅)₄”

Column 9, line 9:

“the nSBt”

Column 12, line 6:

“(1 mmol)”

Column 12, line 42:

“1520 cm⁻¹,”

Column 15, line 9:

“{[XL₂Zn₂(btc),]”

Column 16, line 16:

“space group 14/*mmm*,”

Column 16, line 18:

“-31 ≥ *k* > 31,”

Column 16, line 19:

“-36 ≥ *l* > 21).”

Column 17, line 50:

“in 20 and”

Page 9, Paragraph 0060, line 4:

--carboxylate that--.

Page 11, Paragraph 0075, lines 9 and 10:

--criterion include--.

Page 12, Paragraph 0080, line 6:

--(M₁₆A₁₅)₄--.

Page 12, Paragraph 0082, line 6:

--the nSBU--.

Page 16, Paragraph 00104, line 1:

--(1 mmol)--.

Page 17, Paragraph 00112, line 1:

--1520 cm⁻¹--.

Page 21, Paragraph 00136, line 2:

--{[XL₂Zn₂(btc)₁]--.

Page 22, Paragraph 00136, line 1:

--space group I4/*mmm*,--.

Page 22, Paragraph 00143, line 3:

-- -31 ≥ *k* ≥ 31,--.

Page 22, Paragraph 00143, line 3:

-- -31 ≥ *l* ≥ 21)--.

Page 24, Paragraph 00164, line 1:

-- in 2Θ and--.

JAN 24 2006

Column 20, line 32:

“0.741 nmol)”

Column 22, line 35:

“molecules”

Column 22, line 39:

“1-propanol”

Column 22, line 55:

“one or said”

Page 28, Paragraph 00186, line 1:

-- 0.741 mmol--.

Page 4 of February 16, 2005 Amendment,
original claim 24, (renumbered as claim 22):

--molecule--.

Page 5 of February 16, 2005 Amendment,
original claim 25, (renumbered as claim 23):

--I-propanol--.

Page 5 of February 16, 2005 Amendment,
original claim 54, (renumbered as claim 25)::

--one of said--.

A true and correct copy of pages 4, 7, 9, 11, 12, 16, 17, 21, 22, 24, and 28 of the specification and pages 4 and 5 of the Applicants' February 16, 2005 Amendment as filed that support Applicants' assertion of the errors on the part of the Patent Office accompanies this Certificate of Correction.

Approval of the Certificate of Correction is respectfully requested.

Respectfully submitted,



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JMM/amh

Attachments: pages 4, 7, 9, 11, 12, 16, 17, 21, 22, 24, and 28 of the specification;
pages 4 and 5 of the Amendment dated February 16, 2005.

JAN 24 2006

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,965,026

Page 1 of 2

APPLICATION NO.: 10/083,781

DATED : November 15, 2005

INVENTORS : Michael J. Zaworotko, Brian Moulton

It is certified that errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 3,

Line 39, "subject,invention" should read -- subject invention --.

Column 5,

Lines 44, "J = -350 c⁻¹ and" should read -- J = -350 cm⁻¹ and --.

Column 6,

Line 62, "carboxylate ii that" should read -- carboxylate that --.

Column 8,

Line 21, "criterion g include" should read -- criterion include --.

Line 55, "(M¹₆A¹₅)₄" should read --(M₁₆A₁₅)₄--.

Column 9,

Lines 9, "the nSBt" should read -- the nSBU --.

Column 12,

Line 6, "(1 mmol)" should read --(1 mmol)--.

Line 42, "1520 cm⁻¹," should read --1520 cm⁻¹--.

MAILING ADDRESS OF SENDER:

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JAN 24 2006

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,965,026

Page 2 of 2

APPLICATION NO.: 10/083,781

DATED : November 15, 2005

INVENTORS : Michael J. Zaworotko, Brian Moulton

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Column 15,

Line 69, “[XL₂Zn₂(btc),]” should read -- {[XL₂Zn₂(btc)₁]--.

Column 16,

Line 16, “space group 14/*mmm*,” should read -- space group I4/*mmm*,--.

Line 18, “-31 ≥ *k* > 31,” should read -- -31 ≥ *k* ≥ 31,--.

Line 19, “-36 ≥ *l* > 21).” should read -- -31 ≥ *l* ≥ 21).--.

Column 17,

Line 50, “in 20 and ” should read -- in 2Θ and --.

Column 20,

Line 32, “0.741 nmol) ” should read -- 0.741 mmol --.

Column 22,

Line 35, “molecules” should read -- molecule--.

Line 39, “1-propanol” should read -- I-propanol--.

Line 55, “one or said” should read -- one of said--.

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Line 62, "carboxylate ii that" should read -- carboxylate that --.

Column 8,

Line 21, "criterion g include" should read -- criterion include --.

Line 55, " $(M^1_6A^1_5)_4$ " should read -- $(M_{16}A_{15})_4$ --.

Column 9,

Lines 9, "the nSBt" should read -- the nSBU --.

Column 12,

Line 6, "(1 mnmol)" should read -- (1 mmol) --.

Line 42, " 1520 cm^{-1} ," should read -- 1520 cm^{-1} --.

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Line 32, “0.741 nmol) ” should read -- 0.741 mmol --.

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subtends an angle of 90° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0012] Examples of bifunctional carboxylates that can subtend an angle of 90° are shown in Figures 24A-24C. The angle subtended by the bifunctional carboxylate in Figure 24B is actually 72° , but can sustain distortion to 90° , as determined by molecular modeling experiments.

[0013] Formula 2: $(MA)_{24}$

[0014] Formula 2 represents a general formula for nanoballs (120°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle of 120° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0015] Formula 3: $(MA)_{60}$

[0016] Formula 3 represents a general formula for nanoballs (144°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle of 144° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0017] Formula 4: $(MA)_n$

[0018] Formula 4 represents a general formula for a square (tetragonal) 2D network or lattice of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, A is a bifunctional carboxylate that subtends an angle greater than 90° , and preferably subtends an angle of 120° , allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 4$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0019] Formula 5: $(MA)_n$

[0020] Formula 5 represents a general formula for hexagonal (Kagomé) 2D network or lattice of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry, wherein A is a bifunctional carboxylate that subtends an angle greater than 90° , and preferably subtends an angle of 120° , allowing for geometric distortion, wherein 'n' indicates a polymeric structure, albeit in two dimensions (*i.e.*, $n \geq 3$), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0036] **Figures 11A-11C and 11D-11F** show two further examples, respectively, of networks derived from the crystal structures of the instant invention.

[0037] **Figures 12A-12C** show schematic illustrations of three uniform space filling models based on Platonic and Archimedean polyhedra that are possible for faceted polyhedra.

[0038] **Figures 13A and 13B** show a schematic illustration of how the small cubicuboctahedron and the small rhombihexahedron have a congruent edge-skeleton with the Archimedean polyhedron, the rhombicuboctahedron. In Figure 13A, a rhombicuboctahedron (left) and its edge-skeleton (right) are shown. In Figure 13B, a small cubicuboctahedron (left) and a small rhombihexahedron (right) are shown.

[0039] **Figures 14A and 14B** show an illustration of how the vertices of the molecular squares and triangles are connected by the benzene tri-carboxylic moieties. Molecular squares and triangles are shown in Figure 14A. Only molecular squares are shown in Figure 14B.

[0040] **Figures 15A-15F** show another polyhedra formed containing zinc as the metal in the structure.

[0041] **Figure 16** shows the chemical bonds of a sphere according to the subject invention.

[0042] **Figure 17** shows a distorted version of the molecule of Figures 6A-6J.

[0043] **Figures 18A and 18B** are a schematic representation of triangular and Kagomé lattices, respectively.

[0044] **Figures 19A and 19B** are other representations of square and triangular nSBUs, respectively, that can be formed by linking the vertices of molecular squares.

[0045] **Figures 20A and 20B** show the magnetic properties of the structure described in Example 15. Figure 20A shows the temperature-dependent molar susceptibility (per nSBU), χ , of the structure of Example 15 at a 0.1 Tesla (data points) overlaid by a plot of the Bleaney-Bowers best fit model (solid line): $J = -350 \text{ cm}^{-1}$ and $J' = -18 \text{ cm}^{-1}$. Figure 20B shows the field-dependent magnetization of the structure of Example 15 at $T = 5 \text{ K}$.

[0046] **Figures 21A and 21B** show the magnetic properties of Example 16. Figure 21A shows the temperature-dependent molar susceptibility (per nSBU), χ , of the structure of Example 16 at a 0.1 Tesla (data points) overlaid by a plot of the Bleaney-Bowers best fit model (solid line): $J = -380 \text{ cm}^{-1}$ and $J' = -85 \text{ cm}^{-1}$. Figure 21B shows the field-dependent magnetization of the structure of Example 16 at $T = 5 \text{ K}$.

vertices can be linked via covalent interactions using the coordinating ligands exemplified herein, such as bifunctional or trifunctional carboxylates, as well as other appropriate coordinating ligands. Appropriate coordinating ligands include those angular multifunctional ligands capable of sustaining the desired dihedral angle(s) between nSBUs. Molecular polygons comprising non-metal-organic moieties can be linked at their vertices via non-covalent interactions through bridging ligands. Appropriate bridging ligands include those angular ligands capable of sustaining the desired dihedral angle(s) between non-metal polygons. nSBUs vertices can be linked to vertices of non-metal polygons through bridging ligands, using non-covalent interactions. The appropriate bridging ligands include those angular ligands capable of sustaining the desired dihedral angle(s) between the metal polygon and the non-metal polygon.

[0057] The nanoscale polyhedra of the subject invention can exist as discrete macromolecules or be fused, *e.g.*, in order to crystal engineer open framework solids.

[0058] Examples of general formulas for polyhedron molecules and polymeric structures of the subject invention that are constructed of metal-organic polygons (nSBUs) include:

[0059] Formula 1: $(MA)_{12}$

[0060] Formula 1 represents a general formula for molecules of the subject invention having a spheroid architecture (*e.g.*, nanoballs) (90°), wherein M can be any metal that can sustain 4-fold rotational symmetry (such as a molecular square), A is a bifunctional carboxylate that subtends an angle of 90° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

[0061] Examples of bifunctional carboxylates that can subtend an angle of 90° are shown in Figures 24A-24C. The angle subtended by the bifunctional carboxylate in Figure 24B is actually 72° , but can sustain distortion to 90° , as determined by molecular modeling experiments.

[0062] Formula 2: $(MA)_{24}$

[0063] Formula 2 represents a general formula for nanoballs (120°) of the subject invention, wherein M can be any metal that can sustain 4-fold rotational symmetry (such as a molecular square), wherein A is a bifunctional carboxylate that subtends an angle of 120° (allowing for geometric distortion), and wherein any coordinating ligand or solvent molecule may optionally be coordinated to each M.

4-fold rotational symmetry (such as a molecular square), wherein A is a trifunctional carboxylate with 3-fold rotational symmetry (allowing for geometric distortion), wherein 'n' indicates a polymeric structure in three dimensions (*i.e.*, $n \geq 2$), and wherein any coordinating ligand or solvent molecule is optionally coordinated to each M.

[0074] In each of the above Formulas 2-7, M can be any transition metal and is preferably in its 2+ transition state. It is also contemplated that M can be in other transition states (such as 1+, 3+, and so forth), and structures of the subject invention can contain M in more than one transition state (*i.e.*, M(II)M(III)). For every M that is not in a 2+ transition state, there will preferably exist a counter ion to balance the charge (+ charge if < 2 ; - charge if > 2). The anions may, or may not, be coordinated to the metal.

[0075] Examples of metals that can sustain 3-fold rotational symmetry include, but are not limited to, metals that sustain tetrahedral, trigonal pyramidal, trigonal bipyramidal, or trigonal planar coordination spheres. Examples of first row transition metals (from the periodic table of the elements) that meet this criterion include Zn(II), Cr(IV), Cr(V), Cr(VI), Co(II), Tc(VII), Mn(II), Fe(II), Fe(V), Ni(II), and Cu(II). Preferred metals that can sustain 3-fold rotational symmetry include, for example, Zn(II), Co(II), Ni(II), Fe(II), Cu(II), and Mn(II). Examples of metals that can sustain 4-fold rotational symmetry include, but are not limited to, ions that sustain octahedral, square planar, or square pyramidal coordination spheres. Examples of first row transition metals (from the periodic table of the elements) that meet this criterion include Ti(III), V(III), Cr(II), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II). Preferred metals that can sustain 4-fold rotational symmetry include, for example, Cr(II), Co(II), Fe(II), Ni(II), Cu(II), and Zn(II).

[0076] Bifunctional carboxylates that can subtend an angle of 90° include, but are not limited to, those shown in Figures 24A-24C.

[0077] Bifunctional carboxylates that can subtend an angle of 120° include, but are not limited to, those shown in Figures 2A-2NN. Preferred bifunctional carboxylates that can subtend an angle of 120° include 1,3-benzenedicarboxylate, 5-hydroxy-1,3-benzenedicarboxylate, 5-nitro-1,3-benzenedicarboxylate, and 5-alkyl-1,3-benzenedicarboxylates.

[0078] Bifunctional carboxylates that can subtend an angle of 144° include, but are not limited to, those shown in Figures 3A-3G. Preferred bifunctional carboxylates that can subtend

[0095] The terms “linking moiety”, “linker”, and “spacer” are used herein interchangeably to refer to those moieties which connect vertices of two or more building blocks of the molecular polyhedra of the subject invention, and are intended to be inclusive of the terms “coordinating ligand” and “bridging ligand”.

[0096] The term “coordinating ligand” is used herein to refer to those moieties which connect vertices of two or more metal-organic polygons, such as through covalent interactions.

[0097] The term “bridging ligand” is intended to refer to those moieties which connect vertices of two or more non-metal-organic polygons, or which connect the vertices of a metal-organic polygon and a non-metal-organic polygon, such as through non-covalent interactions.

[0098] The term “0D” is used herein in its crystal engineering sense to refer to a structure that has finite dimensions in all three dimensions (also known as a discrete structure).

[0099] The term “1D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in one dimension and has finite dimensions in two dimensions, such as a string.

[00100] The term “2D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in two dimensions, and finite in one dimension.

[00101] The term “3D” is used herein in its crystal engineering sense to refer to a structure that can be infinite in all three dimensions.

[00102] All patents, patent applications, and publications referred to or cited herein are incorporated by reference in their entirety to the extent they are not inconsistent with the explicit teachings of this specification.

[00103] Following are examples which illustrate procedures for practicing the invention. These examples should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

Example 1—Synthesis of a Discrete Square SBU with Pyridine as Apical Ligand

[00104] Procedure: 0.232 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 4 ml of methanol. An additional solution of 0.244 g (2 mmol) of benzoic acid was dissolved in 4 ml of methanol along with 0.24 ml of pyridine (3 mmol). Both solutions were mixed together very slowly and left to sit under ambient conditions to allow for slow evaporation. After a day or two greenish-blue crystals were formed from the solution.

an angle of 144° include 2,4-pyrroledicarboxylate, *N*-methyl-2,4-pyrroledicarboxylate, 2,4-furandicarboxylate and 1,3-cyclopentadiendicarboxylate.

[0079] Trifunctional carboxylates that can sustain 3-fold rotational symmetry include, but are not limited to 2-, 4- and/or 6-substituted 1,3,5-benzenetricarboxylates. Preferred trifunctional carboxylates that can sustain 3-fold rotational symmetry include 1,3,5-benzenetricarboxylate.

[0080] Additional examples of general formulas for polyhedron molecules of the subject invention that are constructed of metal-organic polygons (nSBUs) include: Formula 8: $(M_4A_3)_2$, which is a tetrahemihexahedron, shown in Figure 10A; Formula 9: $(M_4A_3)_4$, which is a octahemioctahedron, shown in Figure 10C; Formula 10: $(M_7A_6)_4$, which is a small cubicuboctahedron, shown in Figure 10D; Formula 11: $(M_4A_3)_{10}$, which is a small icosihemidodecahedron, shown in Figure 10F; and Formula 12: $(M_{16}A_{15})_4$, which is a small dodecicosidodecahedron, shown in Figure 10H.

[0081] Examples of general formulas for polyhedron molecules of the subject invention that are constructed of non-metal-organic polygons include: Formula 13 (a small rhombidodecahedron): $S_{12}B_{24}$, wherein S is a non-metal molecular square, such as that shown in Figure 27, and B is a bridging ligand, such as that shown in Figure 29; and Formula 14 (small cubicuboctahedron): $S_6T_8B_{24}$, wherein S is a non-metal molecular square, such as that shown in Figure 27, T is a non-metal molecular triangle, such as that shown in Figure 28, and B is a bridging ligand, such as that shown in Figure 28.

[0082] The molecular building blocks of the present invention are preferably, but not limited to, those containing metal-organic moieties (nSBUs). Advantages inherent in the utilization of nSBUs include: (i) metal-organic coordination polymers can be prepared via self-assembly, allowing inexpensive synthesis, often with one step and high yield (*e.g.*, “one pot” reactions); structures having metal-organic nSBUs are inherently modular since they contain at least two components, a node (*e.g.*, the nSBU) and a “spacer” (*e.g.*, a multifunctional organic coordinating ligand); structures having nSBUs can have an open framework, which conveys the ability to gain very precise control over cavities and channels; metal organic coordination polymers are typically of low solubility and, therefore, kinetic and thermodynamic products can be formed for a particular set of components, making them useful for sorption from, and to, solution phases; and metal-organic incorporating structures tend to be moderately thermally stable and air and water stable (many compounds of the subject invention are stable to 200°C and

[00105] Analysis: Crystallography: $a = 10.134$, $b = 10.53$, $c = 17.46$, $\beta = 98.45$, space group: $P2_1/n$, Volm = 1842.94.

[00106] IR Spectrum: intense peak at 1395 cm^{-1} .

[00107] Solubility: soluble in dichloromethane, pyridine, and toluene/pyridine mixture.

[00108] Here, a molecule based on self-assembly of molecular squares formed a small rhombihexahedron by layering of methanolic $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and H_2bdc onto a solution of pyridine that contains templates such as nitrobenzene or 1,2-dichlorobenzene.

Example 2—Synthesis of a Spherical Discrete Crystal

[00109] Procedure: 0.232 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 4 ml of methanol and 3 ml of nitrobenzene. A second solution of 0.166 g (1 mmol) of 1,3-bdc was dissolved in 4 ml of methanol and 0.24 ml of pyridine (3 mmol). After slow diffusion of the 1,3-bdc solution over the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ solution, greenish-blue crystals were formed within hours.

[00110] Analysis: Crystallography: $a = 26.17$, $b = 27.7607$, $c = 28.4356$, $\alpha = 92.719$, $\beta = 96.395$, $\gamma = 92.681$, space group: $P-1$, Volm = 20478.5.

[00111] TGA: around 40% weight loss before decomposition at around 250°C

[00112] IR Spectrum: three intense peaks at 1380 cm^{-1} , 1345 cm^{-1} , and 1520 cm^{-1}

[00113] XPD: broad XPD pattern has been observed

[00114] Solubility: sparingly soluble in common organic solvents but slightly soluble in boiling nitrobenzene.

[00115] The single crystals of $[(L)(S)\text{Cu}_2(\text{bdc})_2]_{12}$, where $L = \text{pyridine}$ and $S = \text{methanol}$, which formed as shown in Figures 5A-5G revealed a structure composed of vertex-linked molecular squares that had self-assembled into small rhombihexahedra. The schematic shown in Figures 5A-5D illustrates how the linking of molecular squares generates the edge-skeleton structure. This molecule contained pyridine ligands at the interior surface that were bonded to the metal ions located at the exterior surface and MeOH ligands at the interior surface metal binding sites. A schematic of this structure is shown in Figure 16.

[00116] It was also observed that the large bowl-shaped square and triangular voids or windows provided access to the interior of the molecule. Disordered solvent was found in these voids or windows and in the 1-nm^3 internal cavity, which was determined to be large enough to

11A-11F and Figures 15A-15F, and the porosities and packing of these structures are also depicted. The basic schematic for Figures 11A-11F is $\{[XL_2Zn_2(btc)_1]_8[L_2Zn_2(btc)_{1.333}]_3\}_n$, where L = pyridine or water, and X = NO_3^- . The schematic representation for Figures 15A-15F is $\{[L_2Zn_2(btc)_{1.333}]_{12}\}_n$, where L = water or pyridine again.

[00137] Another group of compounds is also derived from complexes of the angular trifunctional ligand benzene-1,3,5-tricarboxylate.

[00138] Referring again to Figures 11A-11F, the crystal structure of the compound reveals that it is composed of molecular squares and triangles that were formed by self-assembly into small cubicuboctahedra because two of the btc carboxylate moieties impose a 120° angle at the linkage between the polygons. These have six square faces and eight triangular faces, and the small cubicuboctahedra are fused with one another at the square faces because of the presence of the third carboxylate of each btc ligand. Thus, each square face is fused or shared with the square face of an adjacent small cubicuboctahedron, whereas each triangular face is linked to squares in such a manner that another, smaller polyhedron is generated. This smaller polyhedron is one of the other faceted polyhedra that can be sustained by vertex-linked triangles, which defines an octahemioctahedron. The framework exhibited is low density because the faceted polyhedra are inherently open and, therefore, define a porous structure.

[00139] An aspect of these uniform polyhedra that makes them desirable as nanoscale building blocks is that there is inherently a great deal of control concerning the framework geometries that they must adapt if they close-pack. For example, for combinations of Platonic and Archimedean polyhedra, there exist only eleven possible space-filling infinite frameworks. In addition, there are even greater restrictions for faceted polyhedra since they must pack such that each polygon is connected only by its vertices and does not share its edges. Indeed, the possible packing for faceted polyhedra is restricted to only three related space-filling architectures as shown in Figures 12A-12C: rhombicuboctahedra/cuboctahedra/cubes (1:1:3), as Figure 12A; rhombicuboctahedra/cubes/tetrahedral (1:1:2), Figure 12B; cuboctahedra/octahedral (1:1), Figure 12C.

[00140] Since the small cubioctahedron has a congruent edge-skeleton with a rhombicuboctahedron, as depicted in Figure 13A, it must adapt one of only two possible frameworks. Furthermore, only one of these frameworks can sustain vertex-only connected triangles and squares. It therefore follows that self-assembly of small cubicuboctahedra, or

alternately, self-assembly of triangles and squares by vertex sharing, can result in only one framework. The structure therefore is pre-ordained and, furthermore, is clearly prototypal for other frameworks that can be formed from other molecular triangles and squares. The dimensions of the small cubicuboctahedron are the same as the unit cell dimensions as there is only one small cubicuboctahedron per unit cell. The separation between opposite square faces is therefore 2.05 nm and the dimensions of the windows are approximately 0.9 nm. The overall structure contains channels and cavities that are entirely predictable based on the dimensions of the constituents. It is also noted that the dihedral angle of $125^{\circ}16'$ would exist in a perfect small cubicuboctahedron, as shown in Figures 14A and 14B.

Example 8—Synthesis of a Discrete Crystal (OH-nanoball)

[00141] An OH-nanoball synthesized from the 120 degree dicarboxylate ligand shown in Figure 2B is described below.

[00142] Synthesis: 5g of 5-hydroxyisophthalic acid (27.5 mmol) and 6.39 g of copper nitrate hemipentahydrate (27.5 mmol) was dissolved in methanol (100 ml). 6.40 ml of lutidine (54.9 mmol) was added and the solution was stirred for 15 min under ambient conditions. Addition of diethylether (120 mL) to the solution resulted in precipitation of crude material (10.573 g), crystallization of which from dimethyl sulfoxide afforded the title compound.

[00143] Crystal data: Intensity data collected at 200 K. Tetragonal, space group $I4/mmm$, $a = b = 31.111(4)$, $c = 35.999(6)$ Å, $V = 34844(8)$ Å³, $Z = 2$, $D_c = 0.708$ g cm⁻³, $\mu = 0.778$ mm⁻¹, $F(000) = 7366$, $2\theta_{\max} = 42.08^{\circ}$ ($-30 \geq h \geq 31$, $-31 \geq k \geq 31$, $-36 \geq l \geq 1$). Final residuals (for 296 parameters) were $R1 = 0.1531$ for 5170 reflections with $I > 2\sigma(I)$, and $R1 = 0.2128$, $wR2 = 0.4702$, $GOF = 1.679$ for all 49928 data. Residual electron density was 1.051 and - 0.592 e Å⁻³.

[00144] XPD: Broad peaks

[00145] TGA: Complex weight losses at 36.09, 136.31, 257.14, 334.46, 599.61° C.

[00146] IR (neat, cm⁻¹): 3217.73 (s, OH), 1633.73 (s, carboxylate), 1380.33 (s, carboxylate)

[00147] Solubility: Readily soluble in methanol, ethanol, *iso*-propanol and sparingly soluble in DMF and DMSO.

microcrystals had an average height of 140 nm with a variation of 30 nm; the surface roughness (root-mean-square; RMS) was 56 nm. The average size was 1.3 μm with a variation of 0.4 μm .

[00158] In the case of films prepared on glass, observation on samples that were not thermally treated gave poor image quality even in the non-contact mode due to the presence of residual solvent forming a strongly bound contamination film. This contamination layer was removed by heating to 37° C or 75° C over 24 hours. AFM images of microcrystals on glass after annealing at 37° C and 75° C are shown in Figure 25 and Figure 26, respectively.

[00159] As shown in the figures, the roughness (RMS) is 236 and 261 nm. Image analysis shows an average size of 1.4 μm for the sample annealed at 37° C and again 1.4 μm for that annealed at 75° C, with the variances being 0.4 μm . The average heights were 500 and 600 nm, respectively. For the 37° C sample, the height values were randomly distributed about the average, but in the case of the 75° C sample, there was an apparent statistical distribution of heights at 300, 600, and 900 nm.

Example 12—A Square Lattice Formed From Square SBUs

[00160] Procedure: 0.2326 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1 mmol) was dissolved in 4 ml of water. An additional solution was made by dissolving 0.166 g (1 mmol) of 1,3-bdc in 4 ml of ethanol and 0.24 ml of pyridine (3 mmol). Green crystals were obtained after slow diffusion of the 1,3-bdc solution over the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$.

[00161] Analysis: Crystallography: $a = 18.7912$, $b = 128.7912$, $c = 16.8886$, space group: $P4/ncc$, $\text{Volm} = 5963.5$

[00162] TGA: around 25% weight loss before decomposition at around 280° C

[00163] IR spectrum: intense peak at 1381 cm^{-1}

[00164] XPD: sharp high peak at below 10° in 2θ and some other distinct peaks at above 10° in 2θ

[00165] Solubility: sparingly soluble in common organic solvents.

[00166] An additional embodiment based on the bowl-shaped nanoscale with triangular SBUs is shown in Figures 8A-8C. Again, the generic formula $[\text{Cu}_2(\text{pyridine})_2(\text{bdc})_2]_n$ applies, but the structure corresponds to a semi-regular tiling pattern based on triangles and hexagons, since instead of four units as above, three are used in this case. Because of the nature of the bowl-shaped SBUs and the required connectivity, the hexagons are open and the 2D sheets pack

[00184] The structure described in Example 13 exhibits a different topology, the 2D square lattice that is shown in Figures 7A-7C. In this case, from geometry considerations, spin frustration is ruled out and this is reflected in the magnetic measurements shown in Figures 21A and 21B. To keep the comparison direct and simple, the χ -T and M-H data has been plotted using identical conditions as that of Figures 20A and 20B. These magnetic data are very similar to recent experimental results reported by other groups on Cu₂ dimeric complexes (Zhang, X.X. *et al.* [2000] *J. Appl. Phys.* 87:6007-6009). Theoretical fit using the BB model to the χ -T data in this case yields fit parameters, $J = -380 \text{ cm}^{-1}$ and $J' = -85 \text{ cm}^{-1}$. Of course, the striking feature is the lack of hysteresis for this system with the M-H data exhibiting a straight line representative of a more traditional paramagnetic behavior.

[00185] These results dramatically underscore the potential afforded by supramolecular chemistry for the design of molecular nanostructure assemblies with desirable physical properties and emphasize how the composition of a material is not the only feature one must consider when designing a phase that exhibits molecular magnetism.

Example 17—Polymers Based on Small Cubicuboctahedra

[00186] Procedure: A 10-ml solution of Zn(NO₃)₂·2H₂O (220 mg; 0.741 mmol) and 1,3,5-benzenetricarboxylic acid (220 mg; 1.05 mmol) in methanol was layered onto a 10-ml solution of nitrobenzene containing 0.23 ml of pyridine (2.8 mmol). Large single crystals formed within hours under ambient conditions.

Example 18—Polymers Based on Small Rhombihexahedra

[00187] Procedure: A 10-ml solution of Zn(NO₃)₂·6H₂O (202 mg; 0.679 mmol) and 1,3,5-benzenetricarboxylic acid (126 mg; 0.6 mmol) in methanol was layered onto a 10-ml solution of benzene containing pyridine (0.1 ml; 1.24 mmol). Large single crystals formed within hours under ambient conditions.

[00188] The crystal structure of Example 15, as illustrated in Figures 15A-15F, reveals a compound that consists of small rhombihexahedra, which have congruent edge-skeletons with the rhombicuboctahedron (Figures 13A and 13B), that are fused at the square faces. There is only one possible space-filling arrangement that generates a close-packed framework for these polyhedra, a structure that must be based on squares alone, dihedral angles of 120° (Figure 14B),

17. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim 1,~~
wherein said first or second polygon moiety can sustain 3-fold rotational symmetry.

18. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim 1,~~
wherein said first or second polygon moiety can sustain 4-fold rotational symmetry.

19. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim 1,~~
wherein at least one of said first and second polygon moieties comprises a transition metal.

20. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim~~
19, wherein said transition metal is in a 2+ transition state.

21. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim~~
19, wherein said first and said second polygon moieties each comprise transition metals.

22. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim~~
19, wherein said first and second polygon moieties each comprise transition metals, and wherein said
transition metals are not in the same transition state.

23. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim~~
18, wherein said transition metal is not in a 2+ transition state, and wherein said faceted polyhedron
molecule further comprises a counterion that may or may not be coordinated to said transition metal.

24. (currently amended) The faceted polyhedron molecule ~~or polymeric structure of claim 1,~~
further comprising a solvent molecule.

25. (currently amended) The faceted polyhedron molecule ~~or polymeric structure~~ of claim 1, further comprising a solvent molecule selected from the group consisting of methanol, ethanol, I-propanol, dimethylformamide, and acetonitrile.

26. (canceled).

27. (canceled)

28. (currently amended) A compound comprising a faceted polyhedron molecule ~~or polymeric structure~~, wherein said faceted polyhedron molecule ~~or polymeric structure~~ comprises polygon moieties and linking moieties, wherein said polygon moieties comprise edges and vertices, wherein a first polygon moiety is attached to a second polygon moiety by at least one of said linking moieties, ~~and wherein said at least one linking moiety is attached to a vertex of said first polygon moiety and a vertex of said second polygon moiety; and wherein the faceted polyhedron molecule is~~ a discrete macromolecule.

Claims 29-53 (canceled).

54. (currently amended) ~~The A~~ faceted polyhedron molecule or polymeric structure of claim 1 comprising polygon moieties and linking moieties, wherein said polygon moieties comprise edges and vertices, wherein a first polygon moiety is attached to a second polygon moiety by at least one of said linking moieties, wherein said at least one linking moiety is attached to a vertex of said first polygon moiety and a vertex of said second polygon moiety; and wherein said faceted polymeric molecule or polymeric structure is [(L)(S)Cu₂(bdc)₂]₁₂ or [(S) Cu₂ (bdc)₂]₁₂, wherein L is pyridine, S is methanol, and bdc is benzene-1,3-dicarboxylate.

55. (canceled)